

CHEMICAL COMPOSITION FOR TREATMENT OF NITRATE AND ODORS FROM WATER STREAMS AND PROCESS WASTEWATER TREATMENT.

This application is a continuation-in-part of pending U.S. Serial No. 09/408,834 filed September 30, 1999.

BACKGROUND OF THE INVENTION

Field of the Invention

The present invention relates to nitrates and ammonia removal from process water, or wastewater streams, from mining, agriculture operation facilities, lagoons, military operational facilities, live stockwastewaters, lagoon water systems, and also usually lagoon water having nitrate and metal ions, such as mining operation, suspended solids sludge, and the like. The process to remove the nitrate compromised by adding absorbent, or absorbent-adsorbent products in a solid form, or pellets, or passing the water without pH adjustment, without electropositive metals like aluminum or ferrous or cupric or zinc or iron or mixture ions, which require to have present sulfuric or chlorine or sulfamic acid as well alkali present. The process comprises by processing the water stream, or wastewater's, through the canister or towers having several layers of coagulant-absorbent-adsorbent. The absorbent compositions consisting on products based: (1) on organic modified of sodium bentonite or calcium bentonite or mixture of these, or siliceous volclay, or attapulgite clay, a hydrous silicate of aluminum generated from sodium bentonite or calcium bentonite, cross-linked montmorillonite molecular sieves, porous silicate glass, kaolin surface modified by polycyclopentadiene, tricalcium aluminate, calcium silicate hydrate (comprising by formula $\text{Ca}_6\text{Si}_6\text{O}_{17}(\text{OH})_2$) with bulk density of 85 – 139 g/liter, silica xerogels, high-porosity silica xerogels, crystalline metal-organic microporous materials surface, or surface altered zeolites, or clinoptilolite, zeolite

Analcime (Analcite comprising by formula $\text{Na}_2\text{O} \cdot \text{Al}_2\text{O}_3 \cdot 4\text{SiO}_2 \cdot 2\text{H}_2\text{O}$); (2) with insoluble carbohydrate polymer consisting 25% amylose and 75% amilopectin, a branched-chain structure and having present sulfide or disulfide group, or sulfonated or sulfate groups, or crosslinked starch xanthate, or starch xanthate-xanthide mixture (crosslinked preferably by 2-chloro-N,N-diethylacetamide or epichlorohydrin, sodium trimetaphosphate, phosphorous oxycchloride, formaldehyde, glyoxal, acrolein, and N-methylol urea, or other efficient agents which may give (degree of substitution 0.12 to 0.98), dithiocarbonic acid or xanthate; (3) 3-mercaptopropyltrimethoxysilne or 3-mercaptopropylmethyldimethoxysilane, or 1,3,5-Triazine-2,4,6-(1H,3H,5H)-trithione, trisodium salt, or (4) regenerated cellulose (Ground Viscose) modified NaOH-Diethylaminoethyl chloride hydrochloride) crosslinked with EPI (epichlorohydrin) and exchange capacity of 0.65-0.95 milliequivalents per gram; or (5) Activated Carbon, or anthracite or lignin.

High level of nitrate in ground water can create a serious health risk. The nitrate outflow onto shallow continental shelves can produce nearshore algae blooms. Techniques such as selective ion exchange, reverse osmosis, distillation, elctrodialysis, exist to transfer nitrate between two bodies of water, but only biological process are presently available for nitrate destruction which is very limited, effected by water temperature as well, and very costly as field to be use.

In the United States and Europe, legislation now specifies a maximum permissible nitrate level in drinking water or industrial use waters. Maximum legal nitrate levels in drinking water are 44 mg/liter in United States and 50 mg/liter in Europe. In United States alone the nitrate removal is strongly regulated by EPA, and constitutes serious treat to the water supply.

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The water odor treatment contemplated by this invention is particularly applicable to wastes derived from slaughterhouses, fancy meat departments, and tank houses. The instant method is particularly applicable for reducing odors and contaminants from multi-animal wastewater sources. Current government regulations require that such waste contaminants must be removed from the wastewater, or collected in storage so as to be in compliance with the regulations. The Environmental Protection Agency (EPA) has recently issued very stringent effluent guidelines and standards for hog and poultry industries in particular.

The food processing industries such as the hog industry, poultry industry, slaughter-houses, fish meal factories and bone meal factories typically consume large quantities of water in the various processing segments of their plants, which water is then discharged as wastewater. This water and/or wastewater, contains large quantities of fats and oils, fatty acids, proteinceous material, blood, and other undesirable solids.

The result generally foul smells wastewater that has over 1,000 parts per million (ppm) of total ammonia, over 1,000 ppm of total nitrogen, over 100,000 mg./l. Biological Oxygen Demand (BOD), over 200,000 ppm Chemical Oxygen Demand (COD), over 50,000 ppm of Total Suspended Solids (TSS), and over 30,000 ppm of Oil and Grease (O&G). These levels may vary from plant to plant.

The mining industry, industrial military operations, agriculture industry, is the highly producer of nitrate water stream, nitrate and high concentration metals content in the water stream or lagoons.

Description of the Prior Art

The patent literature suggests different systems for nitrate removal. For example U.S.Patent No. H1,126, Pan et. Al disclose a process comprise adding Sulfamic acid to

the wastewater, in stoichiometric proportion with respect to sodium nitrate, under strict pH control, settling and filtration to form gaseous nitrogen. To use such as system is limited to only small scale, and can not be used to treat large scale or volume of water such as mining and agriculture operations, or lagoons, where are present millions of gallons of waters. This chemical process and its complexity of strict pH control, precipitation, settling and filtration, large sludge volume generate make to be total unpractical for large volume of water treatment.

U.S. Patent No. 5,069,800, Murphy, disclose a chemical process for the denitrification of water comprising treating of water with a metal sufficiently electropositive to decompose the water while regulating the pH in very narrow and its adjustment is a crucial on nitrate reduction (above 9.1-9.3 or to 11.5) range to permit efficient reduction of nitrate ion. By these processes at pH 6.5 to 8 the water is not sufficiently alkaline to start to dissolve for instance aluminum particles and little or not reaction occurs. These processes described are un economical and non efficient for large volume of water to be treated for nitrate removal, and can generate very easily metal cation present in water stream by producing new sources of pollutants. The PAT'126 and PAT'800 are incorporate as reference.

In the other hand, the patent literature reveals that a number of systems have been proposed for clarification of industrial waste effluent of various types of animal waste are described in Waldmann's SN 09/408,834(9/30/99) and incorporated in its entirety by reference.

An aspect of the present invention is that other organophilic clay which may be employed are primary, secondary, tertiary, and quaternary substituted ammonium salts of montmorillonite, hectorite, attapulgite, sepiolite, and semectite in which the substituted

ammonium cation or phosphonium cation contains at least one carbon chain of 12 or more carbon atoms in length. These organically are used in general as thickener agents. The chemically modified clay of the present invention is described on Waldmann's SN 09/408,834(1999), and commercially available. Preferred are the powder forms with smaller particles having low density (Specific Gravity), preferably (1) or less.

None of these aforementioned references teach or suggest the use product compositions having organoclay to remove nitrate or high concentration of nitrate-havy metals present. In contrast, the organoclay described in Serial No. 09/408,834, on present invention composition act as absorbents and adsorbents.

These above listed patents and PAT.APPL. 09/408,834 (1999) is incorporated herein as reference.

Cox, et. Al., in U.S. Patents 5,609,863 and 5,807,587 disclose compositions and methods for reducing odor and septicity by use of one or more aldehydes and/or one or more ketones along with other compounds. '587 also disclose the use of a sulfur and oxygen-bearing component, which is selected from the group of sulfites, metabisulfites, lithium hydrosulfite, and the like. Neither '863 nor '587 teach or suggest that the methods described eliminate the water contaminants or nitrate removal, or nitrate-havy metals mixture. The disclosures of '869 and '587 are incorporated herein as reference.

SUMMARY AND OBJECT OF THE INVENTION

The present invention is a CIP of Serial No. 09/408,834 which discloses a chemical composition and method of treating nitrate water streams, or wastewater streams and associated with nitrate removal, wastewater's nitrate-havy metals mixture removal. More particularly, this invention relates to the use of a combination of: (1) a

clay with the highly synergetic effect of double quaternary ammonium compounds, or mono, or diammonium salts, as chloride, sulfate, carboxylate, bicarbonate, phosphonium salts, or mixture of these with calcium bentonite, sodium bentonite, siliceous volclay, or attapulgite clay, a hydrous silicate of aluminum or magnesium, or surface altered zeolites or clinoptilolite, zeolite Amalcine (Analcite), or crystalline metal-organic microporous materials, or cross-linked montmorillonite molecular sieves, or porous silicate glass, or silicate xerogels or high-porosity silica xerogels, or calcium silicate hydrate (known as Promoxon), in combination with (2) insoluble carbohydrate polymer consisting 25% amylose and 75% amilopectin, with branched-chain structure and having present sulfide or disulfide group, or sulfonated or sulfate group, or crosslinked starch xanthate, or starch xanthate-xanthide mixture (crosslinked preferably by 2-chloro-N,N-diethylacetamide, or epichlorohydrin, sodium trimetaphosphate, phosphorous oxycchloride, formaldehyde, glyoxal, acrolein, and N-methylol urea, (3) 3-mercaptopropyltrimethoxysilane or 3-mercaptopropylmethyldimethoxysilane, or starch xanthate Sulfamic acid adduct, dithiocarbonic acid or xanthate, 3-mercaptopropyltrimethoxysilane or 3-mercaptopropylmethyldimethoxysilane, or 1,3,5-Triazine-2,4,6-(1H,3H,5H)-trithione, trisodium salt, or ground viscose modified (with NaOH-Diethylaminoethyl chloride hydrochloride and crosslinked with EPI (epichlorohydrine).

The clay is selected to be used in connection with this invention as based support, and are described in SN 09/408,834 (6/30/99), and incorporated as reference. The based support can consist on improving physical, mechanical properties of the clay used, from the group of ammonium bentonite organoclay, hectorite cationic clays such as Hectalite, siliceous high swelling Vulco clays (CS-50), non-blue bentonite, and sodium bentonite clays, to calcium bentonite clays, natural or synthetic zeolites, zeolite Analcime

(Analcite), or porous silicate glass, or tricalcium aluminate, or calcium silicate hydrate, or crystalline metal-organic microporous materials, or silica xerogels including high-porosity silica xerogels, or cross-linked montmorillonite molecular sieves.

Another useful base modified clay comprised the use of m Hectorite, or Bentonite, or Hectorite-Bentonite clay mixtures, modified with methyl-dihydrogenated tallow-amine, M2HT (CAS# 61788-63-4) and with a quaternary ammonium compound. For example, quaternary ammonium clays [N(+) $R_{1,2,3,4}$] (Cl⁻) can be modified according to this invention with dihydrogenated-tallowamine, (2HT), as quaternized or protonized are available from Maxichem Inc as MS-0298E₄. These are useful bases, to produce clay modified, and incorporated as reference.

An organic complex based useful for present invention consist on the use of a mixture of high cation exchange hectorite clay (122 meq/g, or 18 parts by weight) with the high swelling sodium bentonite Vulco clay (CS-50, 35 parts by weight), reacted with high alkyl group, or ammonium chloride salt of methyl-dihydrogenated-tallowamine, or M2HT; dihydrogenatedtallowamine, 2HT; and tallow-1, 3-propane diamine, or mixtures of these. Such as products are available from Polymer Research Corporation as MS-0298F19E₅ or MS-0298WW. These products are included as reference.

Another group of products useful as base for the present invention is the organic clay modified from the following group of commercial products:

Very highly charged hectorite clay (120 to 140 meq/g) or a high cation exchanged sodium bentonite (known as Black Hills Bentonite clays) are useful in the present invention.

Products useful also in the present invention as adsorption/ coagulant additives include the following diatomaceous earth products (available from Polymer Reassert

4. Zeolite 20 to 0 parts
5. Insoluble carbohydrate polymer
as high crosslinked yellow starch xanthate 70 to 0.5 parts
(PR-XIS 100)
6. Insoluble carbohydrate polymer crosslinked
Starch xanthate alloy with triazine-trithione
(PR-XIS 210) 0.1 to 70 parts
7. Activated carbon, anthracite or lignin 0.5 to 80 parts

providing that atleast two of the components (1 to 7) are positive, and by the following

Examples:

Example 1. A mixture of an organic clay modified MS-0298E₄ (sold by Maxichem, Inc), high swelling sodium bentonite clay (CS-50) sold by American Colloids, calcium bentonite and insoluble high crosslinked carbohydrate polymer, having present carbon-sulfide or disulfide groups (PR-XIS 100 sold by Polymer Research Corporation as high crosslinked yellow starch xanthate powder) in a ratio of 1:1.2:1:7.00 were milled together in a ribbon blender, or hammer mill to less than 50 microns. The product is available from Polymer Research Corporation under name MS-0298XMT/C in a powder form (tint greenish color and specific gravity of 1.10 g/ml (H₂O=1), or granule form. designated as **(Product A)**;

Example 2. An organic modified clay sold under name of Bentone 34(sold by Rebox, Inc.) is mixed and milled together in a hammer mill, or ribbon blender with high swelling sodium bentonite (CS-50) and PR-XIS 100 in the ratio of 1:1:4.5. The product is available from Polymer Research Corporation under name

MS-0298XMT/A, and is designated as **(Product B)**.

Example 3. A modified organic clay MS-0298MDF19 (described in SN 09/408,834, 1999, available from Polymer Research Corporation) is used as substitute for MS-0298E₄ of Example 1. This is mix with calcium bentonite, MS-XIS 100 and triazine-trithione groups (PR-XIS 210 available from Maxichem, Inc) as high crosslinked yellow starch xanthate powder copolymer) in the ratio of 1.14: 1.14: 1.00: 7.01 and follow the procedure of Example 1. This product is available from Polymer Research Corporation under the name of MS-0298XMT/E, and is designated as **(Product C)**

Example 4. A high swelling sodium bentonite (CS-50), natural zeolite and PR-XIS 100 are mixed in a ribbon blender in the ratio of 1: 8.02: 30.05 and than granulated. This product is available from Polymer Research Corporation under the name MS-0298XMT/CC, and is designated as **(Product D)**.

Example 5. Another embodiment of the present invention consist on mixing in a hammer mill MS—8920F10CAS(as described in Wladmann's SN.09/408,834 of 6/30/99) with MS-XIS 100(described in Example 1) in a ratio of (4.33 to 1.00) and granulated. This product is available from Polymer Research Corporation under the name MS-0298XMT/W designated as **(Product E)**.

Example 6. Another embodiment of the present invention consist on mixing one of the Products A to E with activated carbon (AC) known in the market as Calgon F-400, elf ATOCHEM such as Acticarbhone ENO or CX/H or CXV, or anthracite, or lignin in a weight ratio of (1-: 05): (0.5-1.0) with respect of products ratio to (AC). These products are available from Polymer Research Corporation as powder- palletized under the name MS-0298XMT/WAC designate as **(Product**

F). These product compositions are also compatible with an anionic flocculent such as PR-8633 (available from Maxichem, Inc) and can be use in the powder form or granule, and is called MS-0298XMT/WACF. The product MS-0298XMT/WACF has very good properties as absorbent-adsorbent-coagulant-flocculent in one composition. These products are very useful in special for the nitrate-metals mixture and high metals concentration treatment of wastewater stream.

The MS-0298XMT/WACF is combining such as properties, that leaves a metal-nitrate water stream actually free of nitrate, and heavy metal cations in aqua solution are polish, under limits required by EPA discharged (See Table 2, Nitrate & Metals Removal attached; Test performed by BDL Environmental Technologies).

The superior advantage of this invention is also that the nitrate water stream, or nitrate and havy metal cations present in wastewater, can be treated in batch wise or flow systems (canister having layers with granule of products used) without pH adjustment, or electropositive metals present, or free inorganic acid. For the nitrate removal is follow standard water treatment method described by HATCH/EPA Method No1468-03, and the treatment process of the present invention comprises the following step:

1. Without pH adjustment in a 1000-ml beaker is added 70-PPM standard sodium nitrate at pH and products used and as is stated in Table 1. The media was agitated for 1hr.

The Test Results are summarized in Table 1, Table 2 for Nitrate and Nitrate & Metal Removal, Table 3 Nitrate Removal (Test Results) and Table 4 Test Results

from Hog Farm Wastewater for Nitrogen removal, all tested by BDL
Environmental Technologies of Charleston South Carolina.

Nitrate Removal

TEST RESULTS

TABLE 1

Note: 70 p.p.m. of standard sodium nitrate, without pH adjustment is placed in a 1000-ml beaker and agitated for one (1) hour.

Product Dosage: 0.8 grams
Constituent to be removed: Nitrate

| <u>Product</u> | <u>Constituent Level (mg/L)</u> | <u>Test #1 Reduction (mg/L) (%) (pH)</u> | | | <u>Test #2 Reduction (mg/L) (%) (pH)</u> | | | <u>Test #3 Reduction (mg/L) (%) (pH)</u> | | |
|----------------|---|--|-------|-----|--|-------|-----|--|-------|-----|
| MS-0298XMT/C | 10.0 (1)* | 0.0 | 100.0 | 7.4 | | | | | | |
| MS-0298XMT/C | 70.0 (2)* | | | | 0.0 | 100.0 | 8.4 | | | |
| MS-0298XMT/A | 70.0 (2)* | | | | | | | 0.0 | 100.0 | 8.4 |
| MS-0298XMT/CC | 70.0 (2)* | 0.0 | 100.0 | 7.4 | | | | | | |

(1) Ground water from lock manufacturing company

(2) Ground water from a DOD site

TABLE 2

Nitrate & Metals Removal

TEST RESULTS

| <u>Product</u> | <u>Constituents</u> | <u>Constituent Level (mg/L)</u> | <u>Constituent Reduction (mg/L) (%)</u> |
|----------------|---------------------|---|---|
| MS-0298XMT/CC | Nitrate | 70.0 | 0.0 100.0 |
| | Zn | 200.7 | 0.112 99.9 |
| | Cd | 213.2 | 0.002 99.9 |
| | Pb | 239.2 | <0.004 99.9 |

Note: pH level of the water was 8.4

Nitrate Removal

TABLE 3.

TEST RESULTS

Medium Used: MS-0298XMT/C

| <u>Constituent</u> | <u>Constituent Level (mg/L)</u> | <u>Test #1 Reduction (mg/l)</u> | <u>(%)</u> |
|--------------------|---|---|------------|
| Nitrate (1) | 10.0 | 0.0 | 100.0 |
| Nitrate (2) | 70.0 | 0.0 | 100.0 |
| Nitrate (2) | 70.0 | 0.0 | 100.0 |
| Nitrate (2) | 70.0 | 0.0 | 100.0 |

- (1) Ground water from lock manufacturing company
 (2) Ground water from a DOD site

TABLE 4.

Hog Farm Wastewater - Direct From Hog House

TEST RESULTS

| Medium Used | | MS-0298MDF19 | | MS-0298F19A | | MS-0298F19B | |
|--------------------|---|---|------------|---|------------|---|------------|
| <u>Constituent</u> | <u>Constituent Level (mg/L)</u> | <u>Test #1 Reduction (mg/L)</u> | <u>(%)</u> | <u>Test #2 Reduction (mg/L)</u> | <u>(%)</u> | <u>Test #3 Reduction (mg/L)</u> | <u>(%)</u> |
| Nitrogen | 25,160 | 1,0871 | 95.7 | 879 | 97.1 | 819 | 97.4 |

It is to be understood that the forms of the invention herewith described are to be taken as preferred examples of the same, and that various changes may be resorted to, without departing from the spirit of the invention or the scope of the subjoined claims.